CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

Amendments to the Water Quality Control Plan For the Sacramento River and San Joaquin River Basins

For

The Control of Diazinon and Chlorpyrifos Runoff into the Sacramento-San Joaquin Delta

June 2006 Final Staff Report

Appendix F

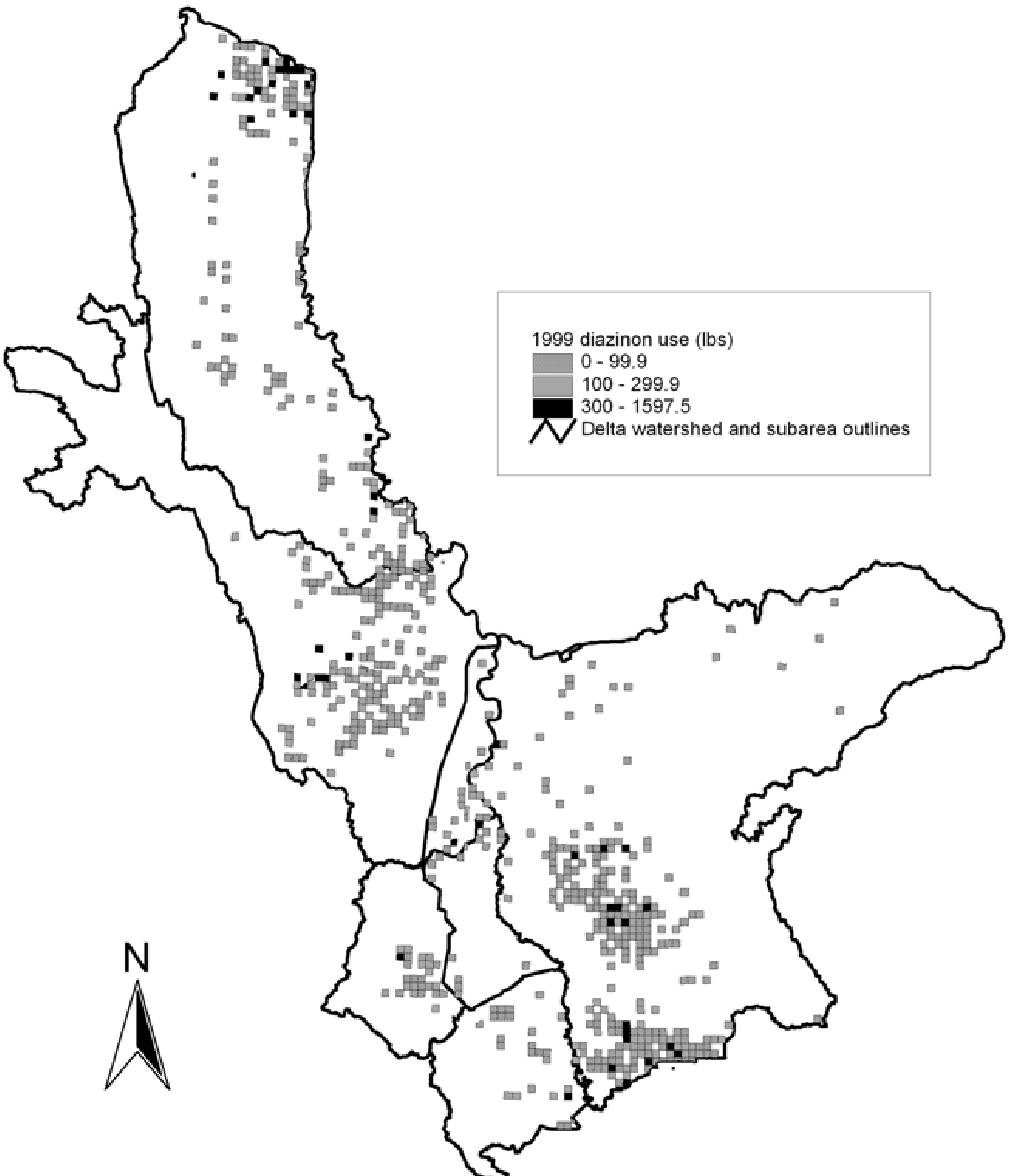
Maps of Total Annual Agricultural Diazinon and Chlorpyrifos Applications in the Delta Watershed 1999-2003, by Year

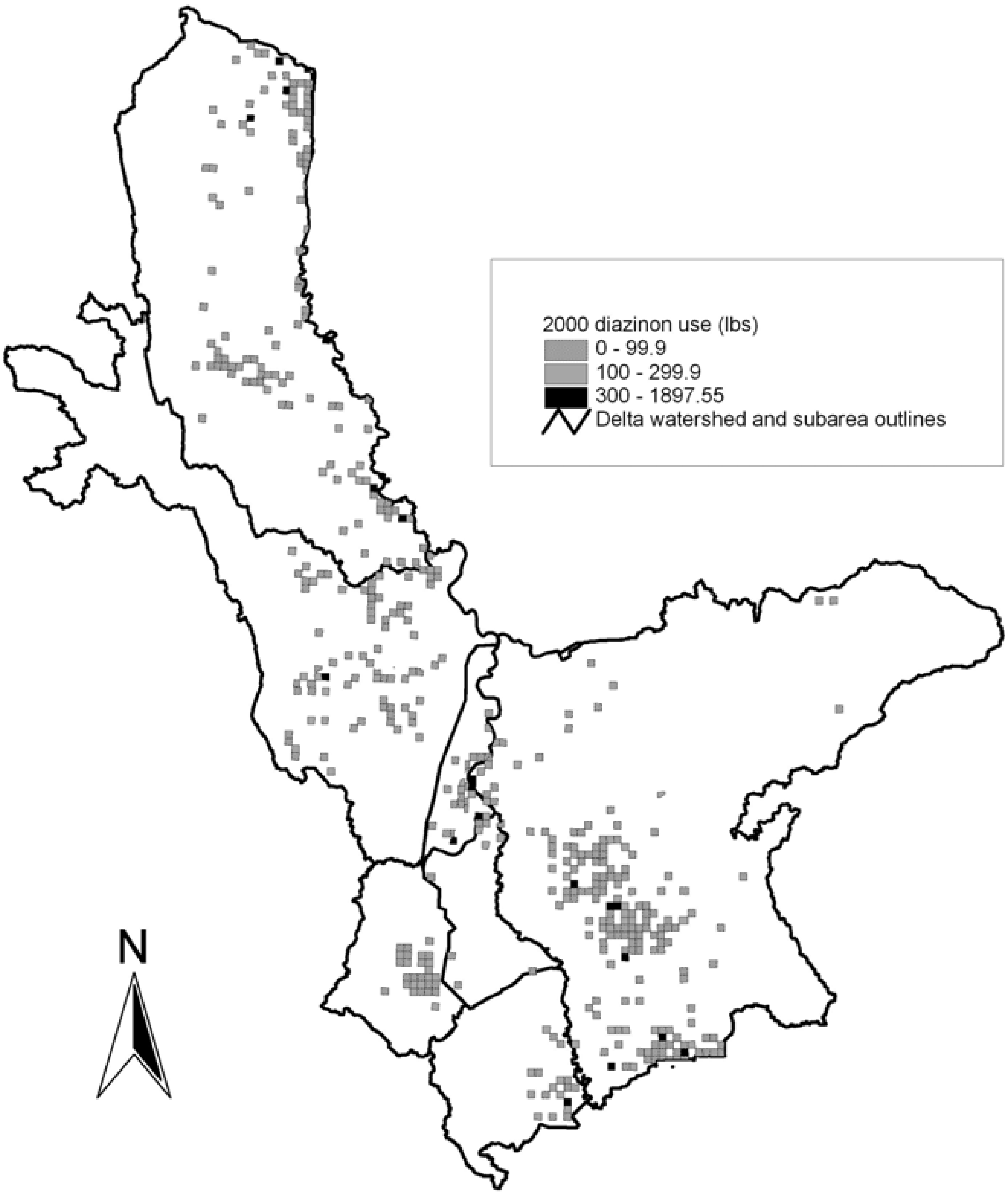
Description

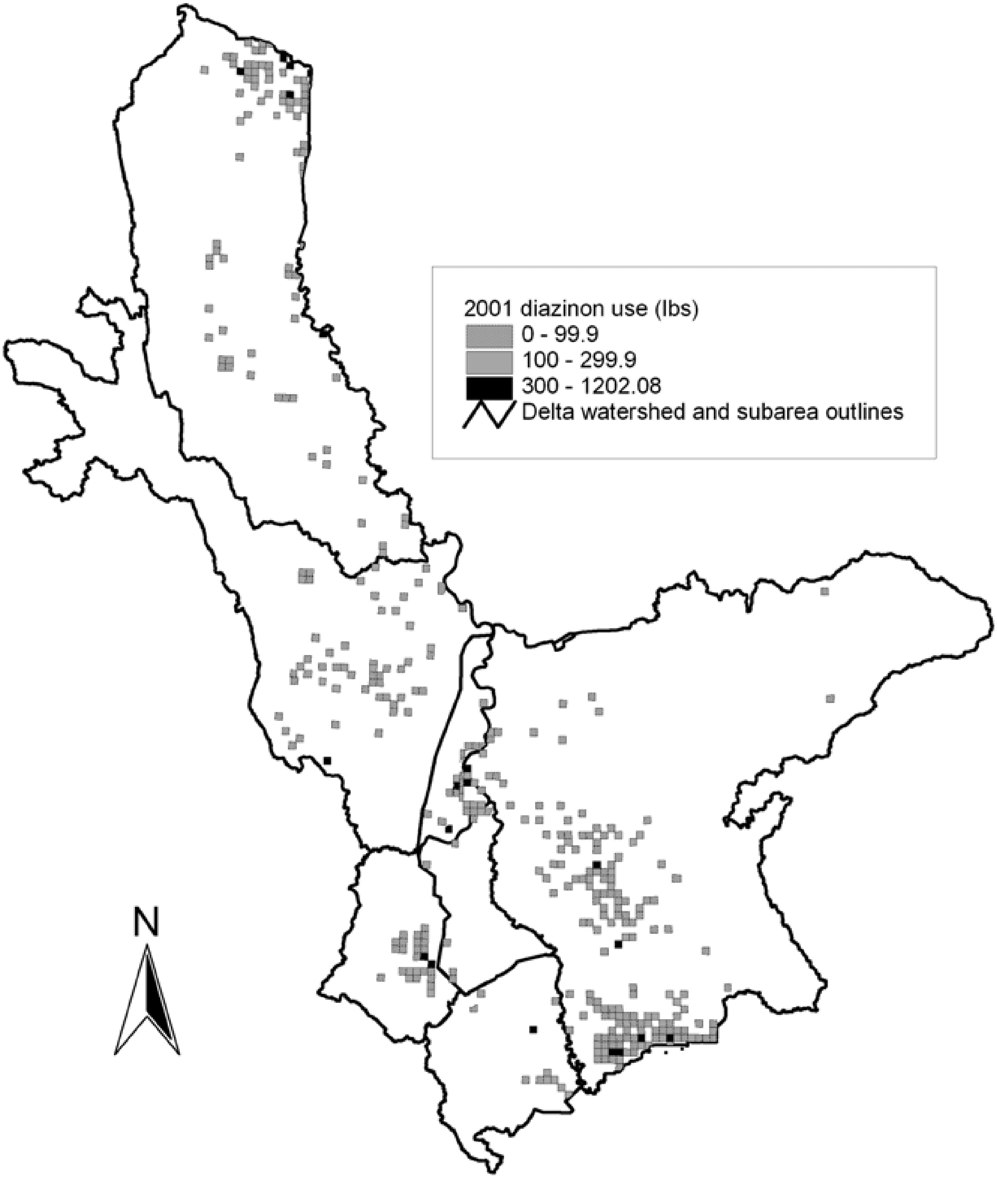
The following figures show the locations of agricultural diazinon and chlorpyrifos applications within the Delta watershed for 1999 through 2003 as reported in DPR's Pesticide Use Report database (DPR, 2005). The outlines of the seven Delta subareas described in Appendix E are included to provide geographical reference. The shaded squares showing application amounts each represent an area of one square mile.

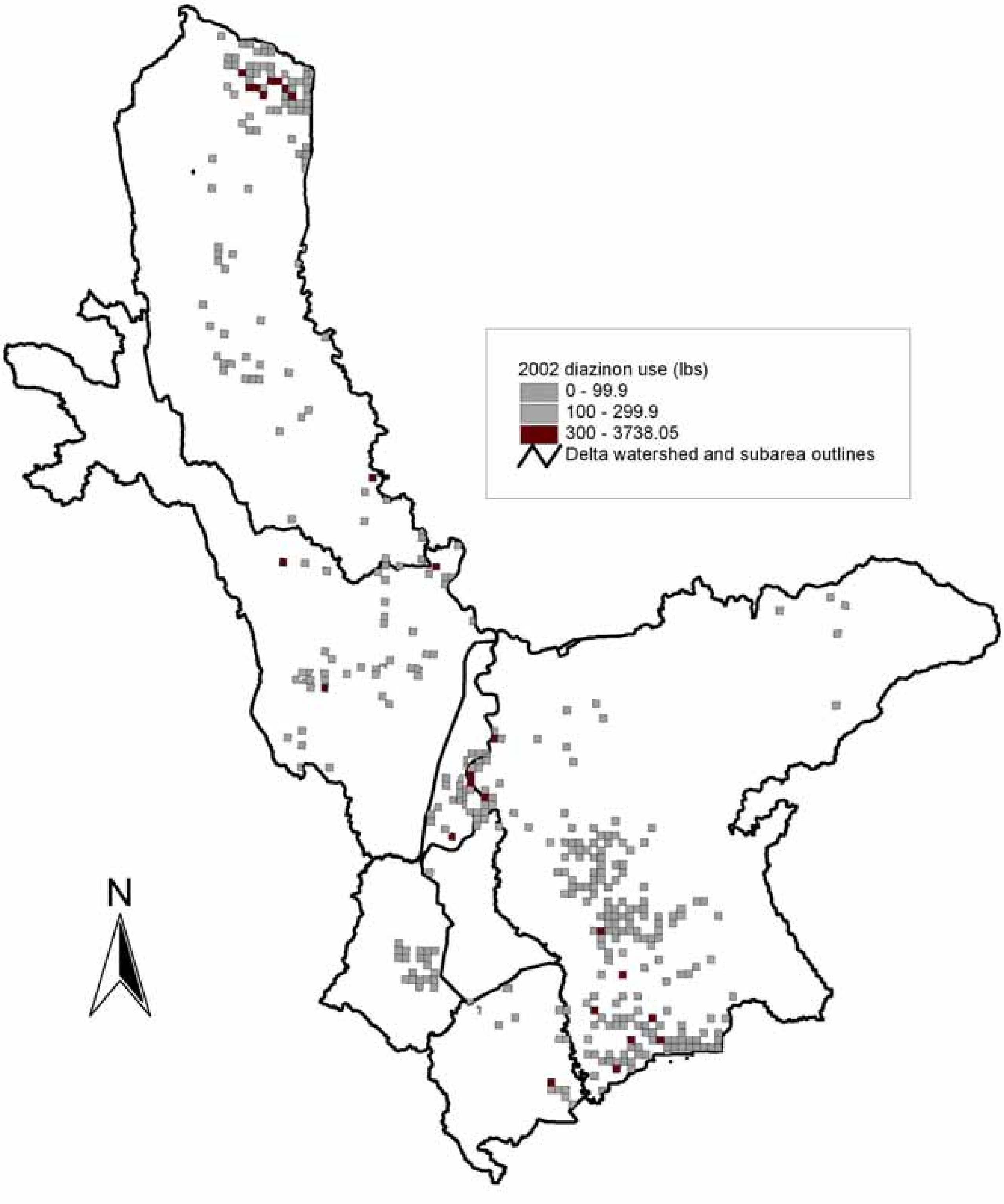
References

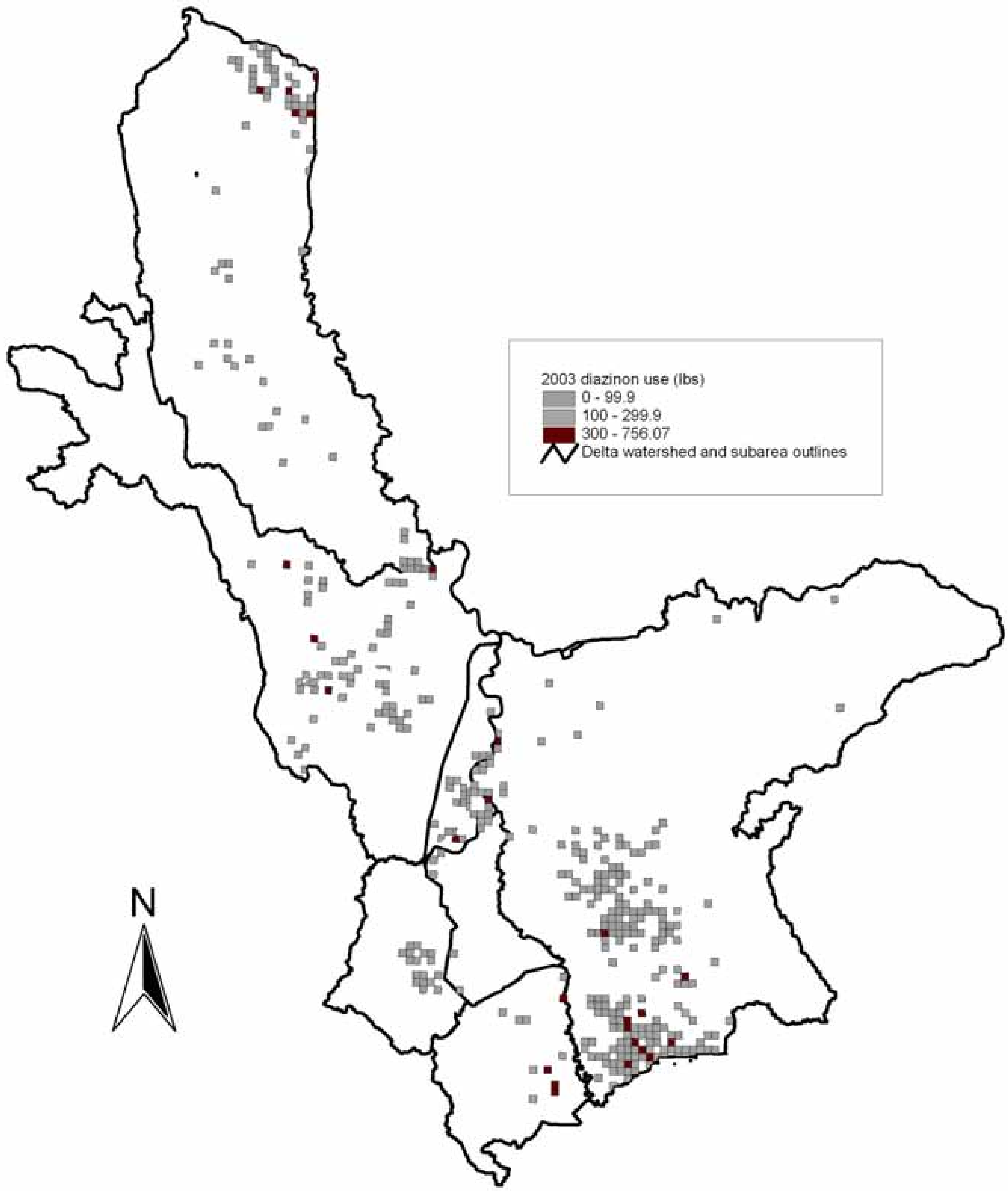
DPR. 2005. Pesticide Use Report Database. California Department of Pesticide Regulations (DPR). Sacramento, CA.


1999 diazinon use (lbs)
0 - 99.9
100 - 299.9
300 - 1597.5
Delta watershed and subarea outlines
N

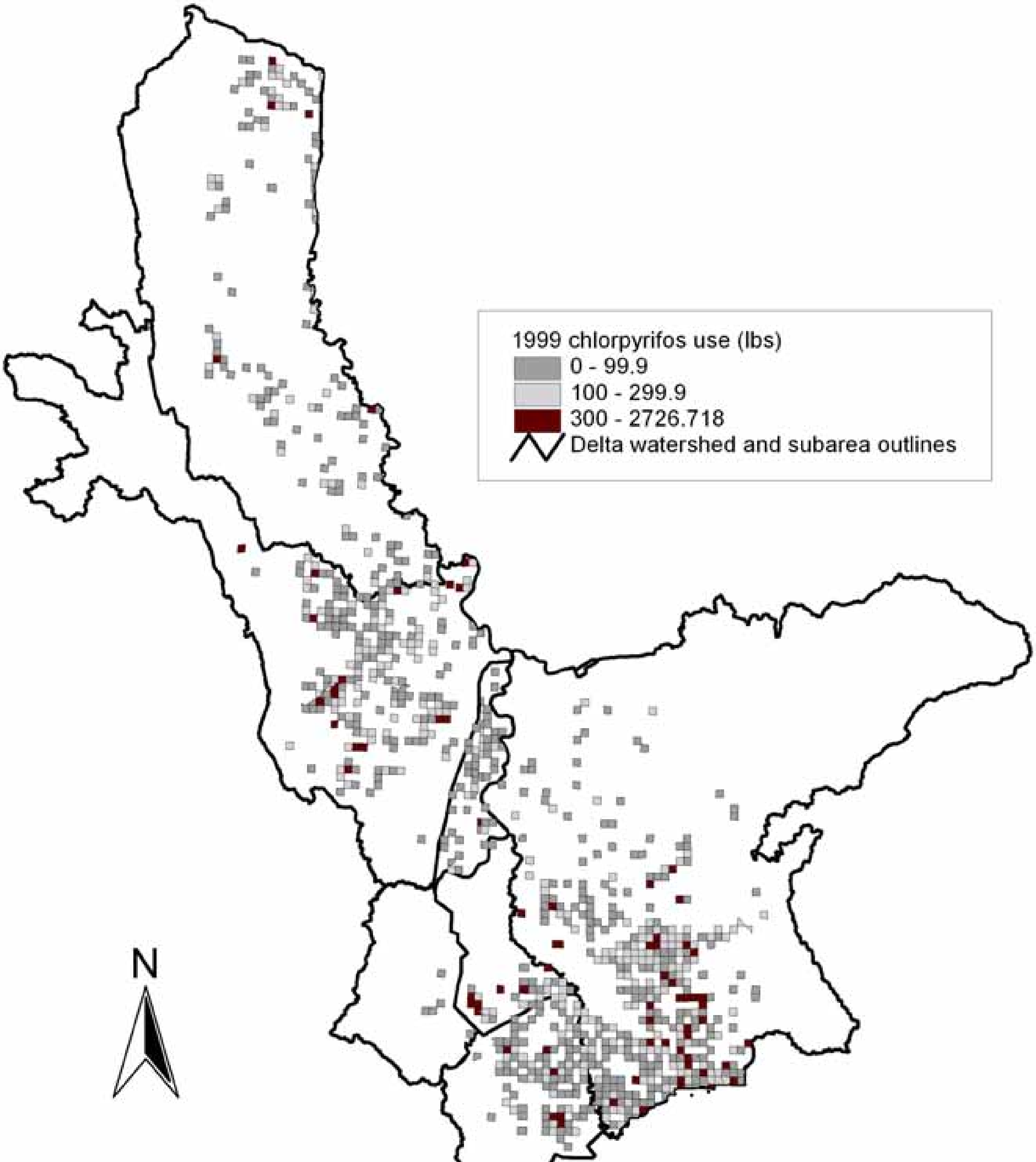

2000 diazinon use (lbs)
0 - 99.9
100 - 299.9
300 - 1897.55
Delta watershed and subarea outlines
N

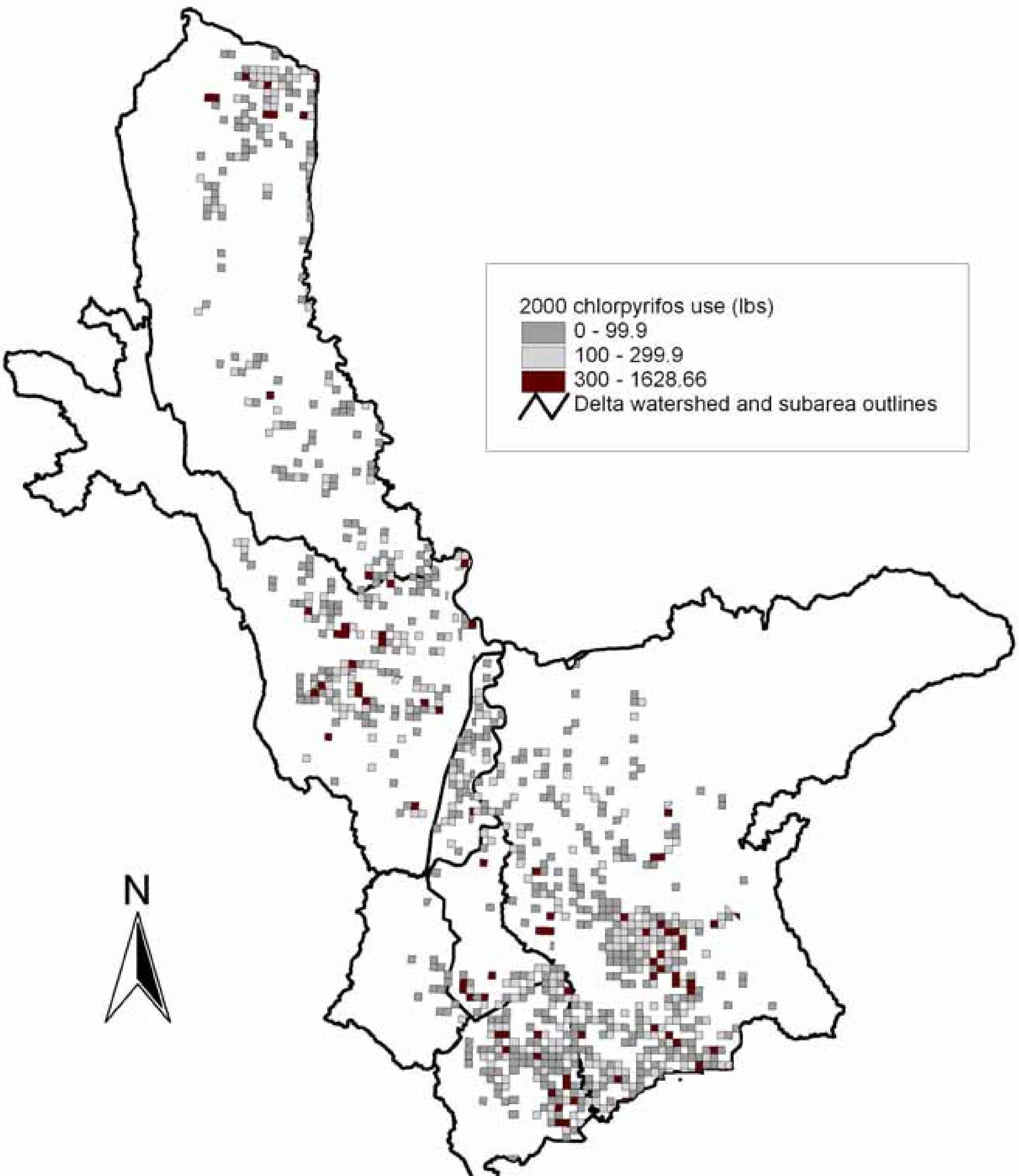

2001 diazinon use (lbs)
0 - 99.9
100 - 299.9
300 - 1202.08
Delta watershed and subarea outlines
N

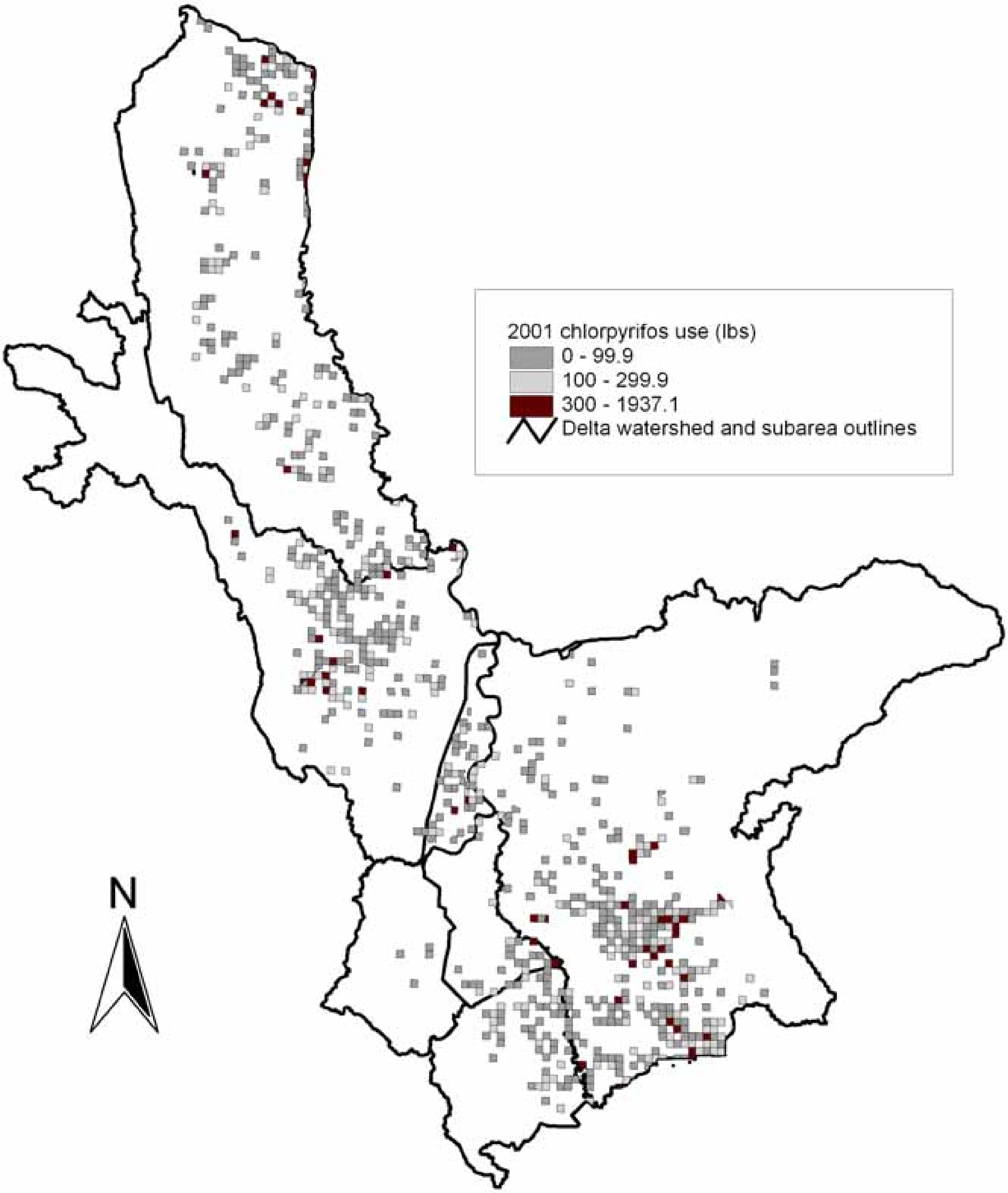

2002 diazinon use (lbs)
0 - 99.9
100 - 299.9
300 - 3738.05
Delta watershed and subarea outlines
N

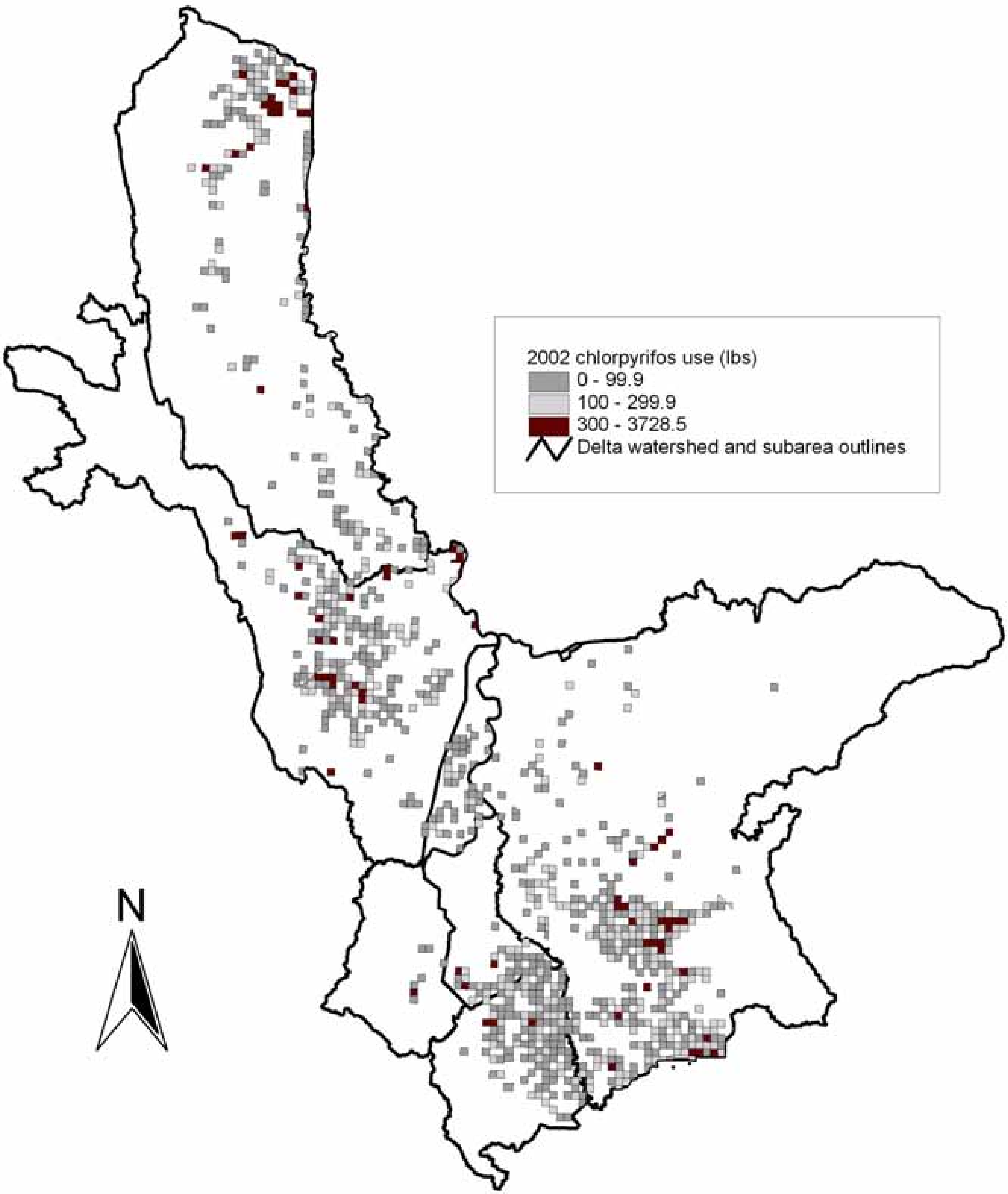


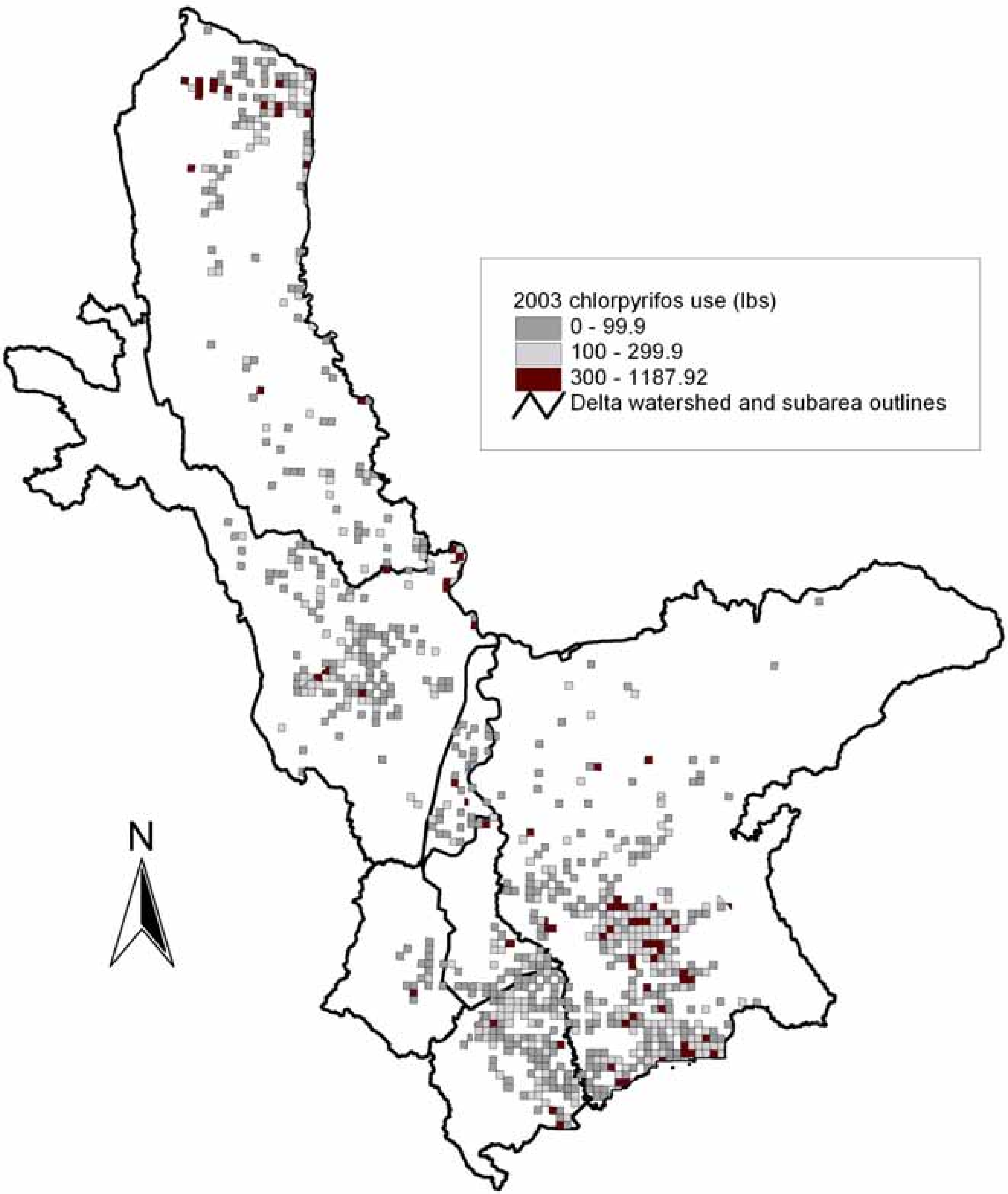
2003 diazinon use (lbs)
0 - 99.9
100 - 299.9
300 - 756.07
Delta watershed and subarea outlines
N


1999 chlorpyrifos use (lbs)
0 - 99.9
100 - 299.9
300 - 2726.718
Delta watershed and subarea outlines
N


2000 chlorpyrifos use (lbs)
0 - 99.9
100 - 299.9
300 - 1628.66
Delta watershed and subarea outlines
N


2001 chlorpyrifos use (lbs)
0 - 99.9
100 - 299.9
300 - 1937.1
Delta watershed and subarea outlines
N


2002 chlorpyrifos use (lbs)
0 - 99.9
100 - 299.9
300 - 3728.5
Delta watershed and subarea outlines
N


2003 chlorpyrifos use (lbs)
0 - 99.9
100 - 299.9
300 - 1187.92
Delta watershed and subarea outlines
N

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Appendix G

Criteria Calculations for Diazinon and Chlorpyrifos

Water Quality Criteria Calculations

This section provides a detailed description of the calculations performed using the USEPA's methodology (1985) for deriving aquatic life criteria. Diazinon criteria were derived using the toxicity datasets (Table G-1) identified as valid by the California Department of Fish and Game (CDFG) (Siepmann and Finlayson, 2000; Finlayson, 2004a) and by USEPA (2005). In performing the diazinon criteria calculations, the *Gammarus fasciatus* study results were removed from both of the CDFG and USEPA data sets, based on the recommendation of Finlayson (2004a) and evaluation of the available *Gammarus fasciatus* data sheets by the Regional Board (CRWQCB-CVR, 2004). Calculations for the complete data set used by USEPA (2005) are also included. The data set used by USEPA (2005) includes *Gammarus fasciatus* acute toxicity values that were changed to a value an order of magnitude higher than originally reported. The chlorpyrifos criteria were derived using the toxicity dataset (Table G-2) identified as valid by the California Department of Fish and Game (Siepmann and Finlayson, 2000).

The USEPA methodology uses only the lowest four Genus Mean Acute Values (GMAVs) directly in the criteria derivation. The total number of GMAVs affects the percentile rankings of the lowest four GMAVs. Table G-3 provides all of the intermediate calculations from application of the USEPA methodology to the four datasets. The intermediate calculations are rounded to four significant figures. The final criteria values are rounded to two significant figures. The number of significant figures for the intermediate values and final criteria follow the USEPA guidelines.

The Regional Board's calculations result in the same diazinon criteria as calculated by CDFG (Finlayson, 2004a). The Regional Board's calculated chlorpyrifos criteria are slightly higher than the CDFG calculated acute criterion (0.025 v. 0.02 μg/L) and chronic criterion (0.015 v. 0.014 μg/L). The differences in the results are likely due to differences in rounding. CDFG rounded the final acute values (FAVs) of diazinon and chlorpyrifos to either one or two significant figures and the Regional Board rounded the FAVs to four significant figures.

Use of the USEPA diazinon data set versus CDFG's data set results in nearly identical FAVs and acute criterion (0.17 v. 0.16 μg/L, respectively). The four lowest GMAVs used by USEPA and CDFG were very similar. The associated percentile ranks were different, since USEPA's data set included additional, less sensitive genera. The inclusion of data for a greater number of genera in the USEPA data set resulted in lower percentile ranks for the four lowest GMAVs, which makes the final criteria higher. The inclusion of the questionable *Gammarus fasciatus* study results in the USEPA data set made no difference in the final results of the criteria calculations.

The difference in the chronic diazinon criterion calculated by USEPA and CDFG (0.17 v. 0.10 μg/L, respectively) is almost completely due to the use of different acute to chronic ratios (ACRs) – an ACR of 2 was used by USEPA and an ACR of 3 was used by CDFG. The ACR calculated by CDFG was preferred, since CDFG included three sensitive species in their calculation of the ACR (versus two by the US EPA contractor) and

CDFG calculated ACRs based on toxicity test results from the same studies or at least the same laboratory.

Table G-1. Diazinon Genus Mean Acute Values Used by CDFG (Siepmann and Finlayson, 2000; Finlayson, 2004a) and USEPA (2005)

USEPA (2005) Data Set		USEPA (2005) Data Set (excluding *Gammarus fasciatus*)		CDFG Data Set Siepmann and Finlayson, 2000; Finalyson, 2004a (excluding *Gammarus fasciatus*)	
Genus Mean Acute Value (μg/L)	**Species**	**Genus Mean Acute Value (μg/L)**	**Species**	**Genus Mean Acute Value (μg/L)**	**Species**
0.3773	*Ceriodaphnia dubia*	0.3773	*Ceriodaphnia dubia*	0.44	*Ceriodaphnia dubia*
0.9020	*Daphnia magna, Daphnia pulex*	0.9020	*Daphnia magna; Daphnia pulex*	1.06	*Daphnia magna, Daphnia pulex*
1.587	*Simocephalus serrulatus*	1.587	*Simocephalus serrulatus*	1.59	*Simocephalus serrulatus*
5.858	*Gammarus fasciatus*[1], *Gammarus pseudolimnaeus*[2]	6.51	*Hyalella azteca*	4.15	*Neomysis mercedis*
6.51	*Hyalella azteca*	10.7	*Chironomous tentans*	4.41	*Physa sp.*
10.7	*Chironomous tentans*	16.82	*Gammarus Pseudolimnaeus*[2]	25	*Pteronarcys californica*
25	*Pteronarcys californica*	25	*Pteronarcys californica*	272	*Lepomis macrochirus*
>50	*Rana clamitans*	>50	*Rana clamitans*	441	*Oncorhynchus clarki Oncorhynchus mykiss*
459.6	*Lepomis macrochirus*	459.6	*Lepomis macrochirus*	660	*Salvelinus fontinalis, Salvelinus namaycush*

[1] In response to the concerns about the questionable toxicity values reported for *Gammarus fasciatus* discussed above, the data set used by USEPA included *Gammarus fasciatus* acute toxicity values that were changed to a value an order of magnitude higher than originally reported (USEPA, 2006).
[2] CDFG found the *Gammarus pseudolimnaeus* study used by USEPA unacceptable for use in calculating water quality criteria because it did not meet ASTM standards for acute toxicity tests (Finlayson, 2004b).

USEPA (2005) Data Set		USEPA (2005) Data Set (excluding *Gammarus fasciatus*)		CDFG Data Set Siepmann and Finlayson, 2000; Finalyson, 2004a (excluding *Gammarus fasciatus*)	
660	*Salvelinus fontinalis Salvelinus namaycush*	660	*Salvelinus fontinalis Salvelinus namaycush*	800	*Poecilia reticulata*
800	*Poecilia reticulata*	800	*Poecilia reticulata*	1,643	*Jordanella floridae*
960.4	*Oncorhynchus clarki Oncorhynchus mykiss*	960.4	*Oncorhynchus clarki Oncorhynchus mykiss*	7,804	*Pimephales promelas*
1,643	*Jordanella floridae*	1,643	*Jordanella floridae*	8,000	*Brachydanio rerio*
3,198	*Pomacea paludosa*	3,198	*Pomacea paludosa*	29,200	*Brachionus calyciflorus*
7,841	*Lumbricus variegatus*	7,841	*Lumbricus variegatus*		
8,000	*Brachydanio rerio*	8,000	*Brachydanio rerio*		
8,641	*Pimephales promelas*	8,641	*Pimephales promelas*		
9,000	*Carassius auratus*	9,000	*Carassius auratus*		
11,000	*Gillia altilis*	11,000	*Gillia altilis*		
11,640	*Dugesia tigrina*	11,640	*Dugesia tigrina*		

Table G-2. Chlorpyrifos Genus Mean Acute Values Used by Siepmann and Finlayson (2000)

Siepmann and Finlayson, 2000	
Genus Mean Acute Value (μg/L)	**Species**
0.06	*Ceriodaphnia dubia*
0.11	*Gammarus lacustris*
0.15	*Neomysis mercedis*
0.38	*Pteronarcella badia*
0.54	*Daphnia magna; Daphnia pulex*
0.58	*Claassenia sabulosa*
0.60	*Chironomus tentans*
0.80	*Petodytes sp.*
3.03	*Lepomis macrochirus*
6.0	*Orconectes immunis*
10	*Pteronarcys californica*
10.1	*Oncorhynchus clarki Oncorhynchus mykiss*
138	*Hyallela azteca*
244	*Salvelinus namaycush*
274	*Pimephales promelas*
475	*Ictalurus punctatus*
>806	*Carassius auratus*
>806	*Aplexa hypnorum*

Table G-3. Results of Calculations Performed by the Regional Board on CDFG Diazinon and Chlorpyrifos Datasets and the USEPA's Diazinon Data Set

Calculation Step	USEPA (2005) Diazinon Data Set	USEPA (2005) Diazinon Data Set (excluding *Gammarus fascitaus*)	CDFG Diazinon Data Set	CDFG Chlorpyrifos Data Set
Rank 1 Cumulative Probability (P) (GMAV- µg/L)	0.0476 (0.3773)	0.0476 (0.3773)	0.0667 (0.44)	0.0526 (0.06)
Rank 2 Cumulative Probability (P) (GMAV- µg/L)	0.0952 (0.9020)	0.0952 (0.9020)	0.1333 (1.06)	0.1053 (0.11)
Rank 3 Cumulative Probability (P) (GMAV- µg/L)	0.1429 (1.587)	0.1429 (1.587)	0.2000 (1.59)	0.1579 (0.15)
Rank 4 Cumulative Probability (P) (GMAV- µg/L)	0.1905 (5.858)	0.1905 (6.51)	0.2667 (4.15)	0.2105 (0.38)
S squared	149.9	162.0	70.21	60.77
S	12.24	12.73	8.379	7.796
L	-3.816	-3.954	-3.043	-4.72
A	-1.079	-1.107	-1.169	-2.977
Final Acute Value(µg/L)	0.3399	0.3305	0.3107	0.0509
Acute Criterion (µg/L)	**0.17**	**0.17**	**0.16**	**0.025**
Acute to Chronic Ratio	2	2	3	3.5
Final Chronic Value (µg/L)	0.1700	0.1653	0.1036	0.01454
Chronic Criterion (µg/L)	**0.17**	**0.17**	**0.10**	**0.015**

The calculation steps are defined below. The cumulative probability (P) and associated GMAVs of the lowest four GMAVs are applied in the equations below.

$$S^2 = \frac{\sum((\ln GMAV)^2) - \frac{(\sum(\ln GMAV))^2}{4}}{\sum(P) - \frac{((\sum(\sqrt{P}))^2}{4}}$$

$$\mathrm{L} = \frac{\Sigma\,(\ln GMAV) - S \cdot \Sigma(\sqrt{P})}{4}$$

$$A = S(\sqrt{0.05}) + L$$

$$FAV = e^A$$

where:

-the Genus Mean Acute Value (GMAV) is the geometric mean of all species mean acute values (SMAVs) for each genus; the SMAV is the geometric mean of all EC_{50} and LC_{50} values for a species.

- the GMAVs are ranked (R) from "1" for the lowest to "N" for the highest; identical GMAVs are arbitrarily assigned successive ranks; and

- the cumulative probability (P) is calculated for each GMAV as R/(N+1)

- the Acute Criterion (Criteria Maximum Concentration) is the Final Acute Value divided by two.

- the Chronic Criterion (Criteria Continuous Concentration) is the Final Acute Value divided by the Acute to Chronic Ratio.

Relative Potency Factor Calculations

The calculation of a “relative potency factor” (RPF) follows the recommendation of Felsot (2005). The purpose of determining an RPF is to normalize the relative potency (or toxicity) of two or more chemicals. In this case, the RPF is calculated to determine the relative toxicity of chlorpyrifos to diazinon. By multiplying the ambient diazinon concentration by the RPF, the diazinon concentrations are normalized to a concentration of chlorpyrifos that would be equivalent in terms of toxicity.

The RPF is expressed in terms of the “Final Acute Value” (FAV) and “Final Chronic Value” (FCV)[3]. The RPF based on the FAV is the Acute Relative Potency Factor (ARPF). The RPF based on the FCV is the Chronic Relative Potency Factor (CRPF).

Equation 1:

$$\text{ARPF}_{\text{(chlorpyrifos/diazinon)}} = \frac{\text{FAV}_{\text{chlorpyrifos}}\ (\mu g/L)}{\text{FAV}_{\text{diazinon}}\ (\mu g/L)} \quad \text{(Acute Relative Potency Factor)}$$

Equation 2:

$$\text{CRPF}_{\text{(chlorpyrifos/diazinon)}} = \frac{\text{FCV}_{\text{chlorpyrifos}}\ (\mu g/L)}{\text{FCV}_{\text{diazinon}}\ (\mu g/L)} \quad \text{(Chronic Relative Potency Factor)}$$

Equation 3:

FCV = FAV/ACR, where the ACR is the “acute to chronic” ratio.

Substituting equation 3 into equation 2 gives:

Equation 4:

$$\text{CRPF}_{\text{(chlorpyrifos/diazinon)}} = \frac{\text{FAV}_{\text{chlorpyrifos}} \times \text{ACR}_{\text{diazinon}}\ (\mu g/L)}{\text{FAV}_{\text{diazinon}} \times \text{ACR}_{\text{chlorpyrifos}}\ (\mu g/L)}$$

Substituting the values in Table 3 into equations 1 and 4, respectively, gives:

$$\text{ARPF}_{\text{(chlorpyrifos/diazinon)}} = \frac{0.0509\ (\mu g/L)}{0.3107\ (\mu g/L)} = 0.1638$$

$$\text{CRPF}_{\text{(chlorpyrifos/diazinon)}} = \frac{0.0509\ (\mu g/L) \times 3}{0.3107\ (\mu g/L) \times 3.5} = 0.1404$$

[3] Note that although Felsot (2005) focused on the acute criteria or endpoints, the approach can also be applied to chronic criteria or endpoints.

Comparison of the "Toxic Equivalents" Calculation Method and the Basin Plan's Method for Considering Additive Toxicity

The section presents the two methodologies considered in establishing the loading capacity of the Delta Waterways for inputs of diazinon and chlorpyrifos. The "Toxic Equivalents" method [Equation 2] is shown to produce the same conclusion regarding attainment of applicable objectives as the method found in the Basin Plan [Equation 1].

The Basin Plan approach is:

$$\frac{C_{diazinon}}{O_{diazinon}} + \frac{C_{chlorpyrifos}}{O_{chlorpyrifos}} = S \leq 1 \quad \text{[Equation 1]}$$

Where:

$C_{diazinon\,=}$ ambient diazinon concentration
$C_{chlorpyrifos\,=}$ ambient chlorpyrifos concentration
$O_{diazinon\,=}$ diazinon water quality objective or criteria
$O_{chlorpyrifos\,=}$ chlorpyrifos water quality objective or criteria

The Toxic Equivalents approach is:

$$\text{ChlorTEQ} = C_{diazinon} \text{ x RPF}_{(Chlorpyrifos/Diazinon)} + C_{chlorpyrifos} \leq O_{chlorpyrifos} \quad \text{[Equation 2]}$$

Where:

$$\text{RPF}_{(chlorpyrifos/diazinon)} = \frac{FAV_{chlorpyrifos}}{FAV_{diazinon}} \quad \text{[Equation 3]}$$

Multiplying both sides of Equation 1 by "$O_{chlorpyrifos}$" yields:

$$\frac{O_{chlorpyrifos}}{O_{diazinon}} \text{ x } C_{diazinon} + \underline{C_{chlorpyrifos}} \leq O_{chlorpyrifos} \qquad \text{[Equation 1a]}$$

Using the USEPA methodology for deriving acute criteria:

$$O_{chlorpyrifos\,=} FAV_{chlorpyrifos} / 2 \quad \text{[Equation 4a]}$$
$$O_{diazinon\,=} FAV_{diazinon} / 2 \quad \text{[Equation 4b]}$$

Substituting equations 4a and 4b into the left hand side of Equation 1a gives:

$$\frac{FAV_{chlorpyrifos}}{FAV_{diazinon}} \text{ x } C_{diazinon} + \underline{C_{chlorpyrifos}} \leq O_{chlorpyrifos} \qquad \text{[Equation 1b]}$$

Substituting Equation 3 into Equation 1b gives:

$RPF_{(chlorpyrifos/diazinon)} \times C_{diazinon} + \underline{C_{chlorpyrifos}} \leq O_{chlorpyrifos}$ [Equation 1c]

Equation 1 (the Basin Plan approach) has been shown to be the same as Equation 2 (the "Toxic Equivalents" approach).

References

Felsot, A. 2005. A Critical Analysis of the Draft Report, "Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Diazinon and Chlorpyrifos Runoff into the Lower San Joaquin River" (Karkoski et al. 2004)

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Appendix H

Responses to Scientific Peer Review Comments

The following discussion presents the comments received from the two scientific peer reviewers and Regional Water Board staff responses follow each comment. Scientific peer review comments were provided on Amendments to the Water Quality Control Plan For the Sacramento River and San Joaquin River Basins for The Control of Diazinon and Chlorpyrifos Runoff into the Sacramento-San Joaquin Delta, January, 2006 Peer Review Draft.

1.1 Comments from Scientific Peer Reviewer Thomas M. Holsen, PhD. Director, Environmental Manufacturing Management Program, Department of Civil and Environmental Engineering, Clarkshon University

[Comment #1]

The Peer Review Draft "Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Diazinon and Chlorpyrifos Runoff into the Sacramento-San Joaquin Delta" is a well-written, well organized report. In general I found the findings well justified and scientifically sound. Two areas of potential concern are listed below in the overarching questions section. Responses to each charge question are given below.

Response to Comment #1
This comment is supportive of the proposal. No further response is required.

[Comment #2]
Issue 1: Use of freshwater water quality criteria as the basis for site-specific water quality objectives.

As indicated in the Peer Review Draft for diazinon the freshwater criteria are more stringent that the saltwater criteria. Therefore adopting the freshwater criteria for all parts of the bay would be protective for diazinon. However for chlorpyrifos the opposite is true. According to the Draft, the salinity used in the toxicity test to derive the saltwater criteria was much higher than found in even the most saline parts of the delta. In addition these saline regions are subject to tidal flushing with water that contains relatively small amounts of chlorpyrifos, and based on the data presented never exceed the proposed criteria. Therefore I believe if is reasonable to use the freshwater water quality criteria for all parts of the bay.

Response to Comment #2
This comment is supportive of the proposal. No further response is required.

[Comment #3]
Issue 2: Application of loading capacity and allocation methodology to a tidal belt.

Since both diazinon and chlorpyrifos are often both present at levels of concern in the Delta Waterways, additive toxicity must be considered in determining loading capacity. To address joint toxicity the equations presented in Section 5.2.8 can be used. There are several options for determining loading capacity, for example a concentration based approach, a mass based approach, a fixed loadings capacity approach or a variable loading capacity approach. Given the hydrodynamic complexity of the Delta Waterway (including tidal flows), the temporal and spatial variability of use, and the temporal variability in rainfall amounts, I think that the only practical approach is the one proposed - a concentration-based loading approach that addresses the additive toxicity of diazinon and chlorpyrifos. This approach is the most straightforward, and easiest to use in assessing compliance.

The proposed load allocation method in which the concentrations of diazinon and chlorpyrifos in all the water coming into the Delta Waterway would be no greater than the concentrations set by the loading capacity is a reasonable approach given the complexities of the Delta Waterway.

Response to Comment #3
This comment is supportive of the proposal. No further response is required.

[Comment #4]
Issue 3: Goals for monitoring to assess compliance with the TMDL and water quality objectives in the Delta Waterways.

The alternative chosen for monitoring “provide general direction on the required monitoring and surveillance” is a reasonable recommendation in that it provides the greatest flexibility to take advantage of the different groups and agencies conducting monitoring and evaluating management practices. It is also consistent with what was recommended for the Lower San Joaquin River. The goals of the monitoring program (p. 90) are appropriate and the challenges in meeting the goals appropriately identified. Particular attention should be paid to water quality in back sloughs. A recent publication found that ecologically important back sloughs had the highest percentage of toxic samples (approximately 15% of the samples tested) (Werner et al., 2000). They also found that toxicity may have persisted over periods of several days to weeks.

The recommendation for monitoring for toxicity is critically important given the likelihood that other pollutants will be present. As is discussed below there is evidence that in the presence of some other pollutants diazinon and chlorpyrifos are more toxic than if they are present by themselves.

Response to Comment # 4

Monitoring in back sloughs and monitoring for toxicity are expected to the meet the proposed monitoring goals #1, 5 and 6, among others. Back sloughs are specifically mentioned under the discussion of monitoring goal #1 in the Staff Report. Additional language has been added to the Staff Report under the discussion of monitoring goal #6 to identify the toxicity monitoring and toxicity identification evaluations that should be used to meet this goal.

Issue 4: Overarching questions.
(a) - Are there any additional scientific issues that are part of the scientific basis of the proposed rule that are not described?
(b) Taken as a whole, is the scientific portion of the proposed rule based upon sound scientific knowledge, methods, practices?

[Comment #5]
Presence of Other Pollutants

The overall plan regulates diazinon and chlorpyrifos as if they were the only pollutants present. However numerous studies have found that a large number of pollutants are found in the Delta. These pollutants can act to increase the toxicity of diazinon and chlorpyrifos. For example Anderson and Lydy (2002) demonstrated that atrazine concentrations as low as 80 µg/L significantly increased the acute toxicity of diazinon to the amphipod *Hyalella azteca*. Belden and Lydy (2000) found a significant increase in diazinon toxicity to the midge *Chironomus tentans* when simultaneous exposure to 40 µg/L of atrazine occurred. Recently atrazine concentrations as low as 5 µg/L in combination with diazinon were found to cause a significant increases in the 48-h acute toxicity of diazinon to C. dubia (Banks et al, 2005). That study demonstrated that combinations of atrazine and diazinon produce greater than additive acute toxicity to *C. dubia* at environmentally relevant concentrations of both pesticides. Greater-than-additive responses were also found for cyanazine in combination with chlorpyrifos, methidathion, and diazinon. Hexazinone increased the toxicity of chlorpyrifos and methidathion to the midge at 200 µg/L by 1.6 and 2 times, respectively (Lydy and Austin, 2004). Recent work that examined the effects of nine commonly detected pesticides in the Delta on the aquatic midge *Chironomus tentans* found that most of the binary mixtures elicited additive responses, however organophosphate insecticides in combination with various herbicides caused greater than additive responses (for example diuron in combination with chloropyrifos and methidathion) (Lydy and Austin, 2004)

> These studies raise questions about the regulation of diazinon and chlorpyrifos using the additive toxicity approach, which inherently assumes they are the only pollutants present. I believe the issue of the presence of other pollutant and their potential affect on diazinon and chlorpyrifos toxicity should be addressed in the Amendments. Requiring toxicity monitoring in addition to individual chemical analysis as suggested is one approach that can be used to at least partially address this issue. As noted in the document, the Basin Plan requires that "No individual pesticide or combination of pesticides shall be present in concentrations that adversely affect beneficial uses."

Response to Comment #5
We agree that the presence of other pollutants that can increase the toxicity of diazinon and/or chlorpyrifos is a concern. The studies cited show increased toxicity of diazinon and/or chlorpyrifos in combination with herbicides that are present in the Delta Waterways, including atrazine, simazine, cyanazine, hexazinone, and diuron. The concentrations of these herbicides found in the Delta (Kuivila et al., 1999) are at least an order of magnitude lower than the levels at which they increased diazinon or chlorpyrifos toxicity in the studies cited. For that reason it is not clear, at this time, how (or if) the potential effects of these herbicides on diazinon and/or chlorpyrifos toxicity should be incorporated into the proposed diazinon and chlorpyrifos water quality objectives and/or loading capacity.

One of the studies cited, Lydy and Austin (2004) also showed additive toxicity when either of the organophosphate pesticides azinphos methyl or methidathion, were combined with diazinon or chlorpyrifos. Since the other organophosphate pesticides are not known to be as significant a concern in the Delta Waterways as diazinon and chlorpyrifos, this Amendment is focused on diazinon and chlorpyrifos. The Regional Water Board is, however in the beginning stages of developing a broader pesticide Basin Plan Amendment to address multiple pesticides that potentially impact Central Valley waterways. Our preliminary water quality risk evaluation (Lu et al., 2006) associated with this broader pesticide Basin Plan Amendment included both azinphos methyl and methidathion and four other organophosphosphate pesticides (diazinon, chlorpyrifos, malithion and methyl parathion) among the "high risk" pesticides. Therefore we will be further examining whether these pesticides need to be addressed, alone or in combination with other pesticides, as part of this broader pesticide Basin Plan Amendment. If necessary, the diazinon and/or chlorpyrifos water quality objectives and/or loading capacity for the Delta Waterways may be revised to include consideration of other organophosphate pesticides as part of that broader pesticide Basin Plan Amendment.

Although other pesticides are not explicitly addressed in this Amendment, the Regional Water Board's Basin Plan currently has water quality objectives that address the combined toxicity of multiple pollutants, and additive toxicity of multiple pesticides. The water quality objectives and loading capacity for diazinon and chlorpyrifos in the proposed amendment in no way usurp the existing objectives. In the proposed Basin Plan

Amendment language, under Diazinon and Chlorpyrifos Runoff into the Sacramento-San Joaquin Delta Waterways, item #7 specifically reads:
<u>"The established waste load and load allocations for diazinon and chlorpyrifos, and the water quality objectives for chlorpyrifos and diazinon in the Delta Waterways represent a maximum allowable level. The Regional Water Board shall require any additional reductions in diazinon and chlorpyrifos levels necessary to account for additional additive or synergistic toxicity effects or to protect beneficial uses in tributary waters."</u>

As noted in the response to comment #4, language has been added to the Staff Report to describe the toxicity monitoring and toxicity identification evaluations that should be used to meet the monitoring goals. If a toxic effect due to multiple pollutants is found to be occurring in the Delta Waterways, this toxicity would need to be addressed under the Basin Plan's currently existing water quality objectives. If future toxicity studies indicate that the diazinon and/or chlorpyrifos water quality objectives and/or loading capacity need to be changed in order to be protective of beneficial uses, appropriate changes can be made in future revisions of the Basin Plan.

> **[Comment # 6]**
> **Importance of Atmospheric Deposition**
>
> The study acknowledges that both diazinon and chlorpyrifos exist in the atmosphere and can undergo both dry and wet deposition, and air-water exchange. Diazinon and chlorpyrifos have been found in rain in the remote Sierra Nevada at concentrations up to 19 and 4.4 ng/L, respectively (McConnell et al., 1998). This finding suggests that atmospheric inputs contribute both diazinon and chlorpyrifos to the Delta. The sources of these pollutants could be both within and outside the Delta watershed. Although atmospheric inputs may not be important to the Delta overall, they may be important in some smaller back sloughs, particularly after long dry periods when dry deposited pollutants can be washed into the Delta with runoff. I think this possibility should be acknowledged and investigated. Some atmospheric monitoring is probably warranted.

Response to Comment #6
We agree that atmospheric deposition and transport of diazinon and chlorpyrifos is a concern in the Delta watershed. Additional language has been added to Section 2.2 of the Staff Report to acknowledge the potential importance of atmospheric deposition. Atmospheric deposition tends to be correlated to proximity to application areas as well as the timing and amount of pesticide used (Majewski et al., 2005). This would indicate that most of the diazinon and chlorpyrifos that ends up in Delta Waterways is from local use in and around the Delta. If diazinon and/or chlorpyrifos concentrations are still found to be at levels of concern after the implementation of management practices by dischargers in the Delta Watershed, atmospheric monitoring may be necessary in some areas.

1.2 Comments from Scientific Peer Reviewer Allan S. Felsot, Ph.D. Professor and Extension Specialist, Department of Entomology, Washington State University & College of Agriculture Food & Environmental Quality Lab.

[Comment #1]
Introductory Comments:
To support a TMDL for diazinon and chlorpyrifos entering the Sacramento-San Joaquin Delta, McClure et al. have followed a similar analytical strategy as presented in Beaulaurier et al. (2005) for the control of the subject insecticides in the lower San Joaquin River. Thus, McClure et al. chose to use the same short-term (acute) water quality objectives of 0.16 µg/L (160 ng/L) for diazinon and 0.025 µg/L (25 ng/L) for chlorpyrifos. The chronic water quality objectives of 0.10 µg/L or diazinon and 0.15 µg/L for chlorpyrifos are also consistent with the lower San Joaquin River objectives. Although the chronic objectives are not specifically used in further analyses to determine the rate of current compliance at the various sampling stations, McClure et al. did an analysis using the alternative objectives of 0.042 µg/L for diazinon and a hypothetical 0 µg/L for chlorpyrifos. Nevertheless, the rationale for choosing the stated water quality objectives was detailed well in Beaulaurier et al. (2005) and further discussed in comparison with alternative water quality objectives, and therefore this reviewer has no disagreement with using them as a basis for implementing risk management programs. They are conservative and do allow for a margin of safety that is consistent with EPA methodology deployed for characterizing risk of pesticides under FIFRA (Federal Insecticide, Fungicide and Rodenticide Act).

McClure et al. have detailed well the seven geographic subareas of the Delta and the usage of diazinon and chlorpyrifos. For the various sampling stations within each subarea, historical and most current residue detections are tabulated. To determine the extent of compliance necessary to reach the water quality objectives McClure et al. have combined the residues of diazinon and chlorpyrifos using the additivity formula presented in Beaulaurier et al. (2005). The rationale for this formula (largely based on the research presented by Bailey et al. 1997) and a response to the critique by this reviewer (Felsot 2005) was detailed in Beaulaurier et al. (2005).

Response to Comment #1
This comment is supportive of the proposal. No further response is required.

[Comment #2]
Issue 1: Use of the freshwater water quality criteria as the basis for site-specific water quality objectives

Owing to the tidal flux of water in the Delta and consequently the dynamics of salinity changes, McClure et al. necessarily explained their rational for relying on freshwater water quality objectives and not altering them to account for the dynamic flux in water chemistry. McClure et al. make their proposal in the context of the CDFG saltwater criteria being <2-fold lower than the freshwater criteria for chlorpyrifos, and the absence of a CDFG proposed diazinon criteria (Siepmann and Finlayson 2000). On the other hand, EPA recently finalized for diazinon a saltwater ambient water quality criterion of 0.82 µg/L (EPA 2006).

McClure et al. use two lines of reasoning to support only using the freshwater criteria. First, they cite information from Siepman and Finlayson (2000) indicating that the saltwater tests analyzed to develop a criterion for chlorpyrifos deploy a salinity approximately 10 times higher than the salinity of the western Delta region. Thus, McClure et al. suggest the tests are not applicable to the situation in the Delta. Second, they reason that the incoming tidal flow would have extremely low amounts of diazinon, if any, and therefore would not be contributing to the diazinon load coming from the eastern part of the Delta. Indeed, the tidal flows would dilute the concentrations of diazinon coming from the upriver portions of the Delta. Thus, meeting the freshwater objectives in the upriver Delta would not pose any additional risk to the lower areas owing to the dilution effect.

The issue of the necessity to set different water quality objectives based on saltwater presence has been addressed in the scientific literature from a couple of perspectives. One perspective is to examine the species sensitivity distributions to determine the ratio of toxicity endpoints (typically the LC50 or NOEC) between freshwater and saltwater organisms. Such analyses have been conducted on large sets of many types of chemicals but have also been broken down by specific groups like pesticides (Hutchinson et al. 1998; Wheeler et al. 2002). An examination of a European aquatic toxicity database revealed for the 10 pesticides studied that 90% of fresh to saltwater comparisons among fish species yielded a ratio <10 (Hutchinson et al. 1998). The two OP insecticides in the database, malathion and chlorpyrifos, had freshwater to saltwater fish ratios of 5.9 and 26.3, respectively. No OP insecticide data was presented for the invertebrate toxicity tests.

The use of the HC5 is another approach for comparing the sensitivity of freshwater and saltwater species toward a diverse group of chemicals. The HC5 is the hazardous concentration for 5% of the species based on a species sensitivity distribution of LC50s and statistical unction fitting. In other words, the HC5 represents an LC50 value protective for 95% of species in the database. For 21 species in the EPA ACQUIRE toxicology database, the saltwater HC5 was 5.5 fold less than the freshwater HC5 (Wheeler et al. 2002), which was an estimate in approximate agreement with the European findings (Hutchinson et al. 1998). For malathion, the freshwater and saltwater HC5s were 2.472 and 0.979 µg/L, respectively. For chlorpyrifos, the freshwater and saltwater HC5s were 0.063 and 0.0064, respectively.

The situation in estuaries involves organisms of the same species experiencing daily changes in salinity. Thus the most relevant studies are those wherein a single organism is exposed to a chemical at different salinities. Such studies have been reviewed for a large variety of chemicals including different pesticide classes (Hall and Anderson 1995). Although no consistent trend was found in changes in toxicity of organic chemicals as salinity changed, the OP insecticides were an exception. Of 10 OP insecticides reviewed, 6 compounds exhibited either no correlation or a negative correlation, but 11 compounds were more toxic as salinity increased. Neither diazinon nor chlorpyrifos were among the compounds reported. Most of the salinities studied ranged from 5 to >20 ppth, and thus the applicability of these studies to the Delta are uncertain.

Nevertheless, it is clear that salinity does in general tend to increase toxicity of many OP insecticides, but diazinon is clearly an exception based on the analysis of data presented in Siepmann and Finlayson (2000). Based on environmental chemodynamic principles, the water solubility of hydrophobic compounds tends to decrease as salt concentration increases (Felsot and Dahm 1979). This change could make the compounds more bioavailable by enhancing diffusion rates across gill membranes or invertebrate integuments. On the other hand, this hypothetical increase in bioavailability would be offset by increased sorption to either sediments or suspended organic matter. Given that toxicity studies from which the water quality criteria are derived from tests that use water without added organic matter, they likely overestimate toxicity in natural waters. Therefore, the incremental increases in toxicity with salinity changes are unlikely to have any measurable impact under field conditions.

In conclusion, McClure et al. have duly recognized the increased sensitivity of saltwater aquatic invertebrates to chlorpyrifos compared to freshwater species, but they argue convincingly that two separate criteria are not needed. The tidal dilution effect is very significant, and the salinity ranges used to test how a single species might react to changes in salt content are much higher than what is likely occurring in the western part of the Delta. Thus, the proposal to have only one water quality objective for chlorpyrifos seems scientifically sound.

Response to Comment #2
This comment is supportive of the proposal. No further response is required.

[Comment # 3]
Issue 2: Application of the loading capacity and allocation methodology to a tidal delta

The Delta draft amendment uses the same approach as the final amendment for the lower San Joaquin River (Beaulaurier et al. 2005). Both amendments eschewed an attempt to distribute percentage loads of pesticides from different geographic subareas as was presented in the Sacramento-Feather River amendment (Karkoski et al. 2003). To calculate a mass load, the flow rate and the concentration of pesticide must be estimated. While flow rates are reasonably predictable based on accumulated meteorological and hydrogeological information, concentrations are very unpredictable owing to the plethora of variables affecting edge-of-field losses. Thus, allocations of mass loads to circumscribe a TMDL are highly uncertain.

In contrast to expressing the TMDL as a mass loading capacity, knowing the dynamics of pesticide concentrations is more relevant to the narrative goal of “no toxicity” and thus more consistent with existing regulations. Organisms “experience” a concentration of pesticides, and bioavailability through a diffusive mechanism is concentration driven. Thus, it is much more logical to gauge progress in improving water quality through monitoring of pesticide concentrations than to try to monitor mass loads.

Furthermore, using a mass loading capacity objective would not reflect properly the tidal dilution effect. For example, because mass load is flow times concentration, the increase in water volume due to dilution does not change the total mass of pesticide in the Delta. However, the concentration, and thus the potential toxicity, should markedly decrease. For this reason, the use of a concentration based TMDL is logical for the Delta and is thus adequately protective.

Response to Comment #3
This comment is supportive of the proposal. No further response is required.

[Comment #4]
Issue 3: Goals for monitoring to assess compliance with the TMDL and water quality objectives in the Delta waterways

The draft amendment considered three alternatives for surveillance and monitoring and favored alternative (2). Alternative (2) would provide guidelines for required monitoring and surveillance but allow flexibility in implementing a program that is tailored to the specific geographical region or landscape. Alternative (2) would be implemented to meet seven monitoring goals, but the first goal of determining compliance with established water quality objectives and loading capacities encompasses a number of the other goals (for example, goals 2, 3, and 4). For goal 1, the draft plan favors option B, monitoring a representative number of Delta waterways rather than numerous unique waterways. Of course, guidelines would have to ensure that the chosen monitoring stations and times of sample collection were representative of the dynamic discharge patterns and hydrological conditions influential on water quality parameters.

Alternative (2) in combination with option B (under goal 1) is essentially similar to the historical and contemporaneous method of monitoring used to judge the necessity of developing a TMDL for diazinon and chlorpyrifos. In other words, the locations of the monitoring stations seem representative of Delta waterways, and the samples have been timed to reflect a dormant spray and irrigation seasonality. Because these established monitoring stations have served as points of reference in establishing degree of compliance with the proposed TMDL, and the percentage reduction in pesticide concentrations needed to meet it, the most logical monitoring plan would be to continue sampling and analysis at these stations.

Response to Comment # 4
We agree that the continued monitoring at the current and historical monitoring stations would provide useful data, especially as points of reference for measuring progress in reducing pesticide concentrations and aquatic toxicity. However, those sites were chosen within the context of the individual studies being performed and the budgetary and logistical constraints on those studies. Therefore, future monitoring may need to be performed at stations that differ somewhat from the stations listed in the Staff Report in order for such monitoring to be representative of all the different discharges and hydrologic conditions of the Delta Waterways.

[Comment #5]
The proposed plan, however, should not preclude providing a strong incentive for agricultural dischargers to show progress in implementing management practices recommended for meeting the TMDL requirements. One incentive might be to require producers to provide monitoring data from a greater number of waterways at a greater sampling frequency if best management practices are not implemented. Producers have many options for implementing management practices as listed in the draft amendment, so BMPs in lieu of monitoring seems a good trade-off. After

all, the ultimate goal should not be reaching a specified numeric target concentration of pesticides but rather to implement ubiquitously practices promoting environmental stewardship.

Response to Comment #5

Under the proposed amendment, monitoring would need to provide enough data to meet the monitoring goals described. This does not preclude reducing the number of monitoring stations if growers are successful in reducing pesticide concentrations through the use of management practices.

[Comment #6]

Regarding goal 5, alternative pesticides and water quality, it is reasonable to first monitor changes in use patterns rather than make any recommendations for monitoring of alternatives. Although several more years will be required to get a reasonably accurate assessment, the main concern will be examining pyrethroid use. An examination of the UC-Davis IPM recommendations suggests that pyrethroid insecticides are not necessarily a substitute for the OP insecticides in dormant spraying. Pyrethroids may be more problematic during the irrigation season. Thus, a need to monitor for pyrethroid toxicity (or sediment concentrations) may not require year long monitoring as does OP insecticide use. Substitution of any other insecticide than pyrethroids for diazinon and chlorpyrifos would not be problematic because chlorpyrifos is much more toxic. If usage rates are the same or even less, there is no reason to hypothesize that toxicity problems would be any greater with the use of alternatives.

Response to Comment #6

Recent pesticide use data (DPR, 2005) indicates that pyrethroids are being used in the dormant season. Therefore pyrethroid monitoring may be necessary in the dormant season as well. Toxicity testing is needed to verify the presence or absence of any potential toxic effects of these alternative products in the Delta Waterways. Adjustments to the timing and amount of toxicity monitoring can be made based on a review of monitoring results.

[Comment #7]

Regarding goal 6, determining additive or synergistic effects, the discussion contained in Felsot (2005) is germane and should be reiterated. While concentrations of co-occurring compounds with identical modes of biochemical action are known to be additive, the appearance of joint toxicity has been shown only to occur above a certain threshold. Thus far for aquatic organisms, co-occurrence of OP insecticides at levels that are significantly below the LC50 do not seem to be additive. To be conservative, however, the proposed amendment does have a formula to allow additivity for co-occurring residues, and from a risk management perspective this application is reasonable. However, the water quality objectives reflect a probabilistic examination of species sensitivities and thus are quite protective of just about every aquatic invertebrate in the toxicity databases. Further concerns about additivity with other contaminants seem inappropriate at the prevalent residue levels of the subject OPs.

If synergism is a concern, then antagonism should also be considered as a likely hypothesis, yet it seems to be ignored. However, synergism, as well as additivity or antagonism, is predictable based on pharmacokinetics and pharmacodynamics. In those studies that suggest synergism between OPs and other pesticides, the concentration of the secondary compound is typically unrealistically high. For example, the concerns about synergism seem to emanate from studies of OP insecticides and atrazine (for example, Pape-Lindstrom and Lydy 1997; Anderson and Lydy 2002). Atrazine concentrations ranging from 40 to 20,000 μg/L had a potentiating (not synergistic) effect on two invertebrate species. Pertinently, no potentiating effect (i.e., the interaction was neutral) occurred at an atrazine concentration of 10 μg//L (Anderson and Lydy 2002), a concentration even rare in the Corn Belt, where herbicide use (especially atrazine) dominates all pesticide usage. Thus, in orchards wherein herbicide applications are likely limited to tree rows, herbicide runoff is less problematic than insecticide runoff and resulting surface water concentrations will be very low if detectable at all. In conclusion, if appropriate BMPs are implemented to prevent OP insecticide translocation to surface waters, then the issue of additivity and synergism is mute and no additional testing or monitoring for synergistic interactions should be required.

Response to Comment #7

The Delta Waterways often have multiple co-occurring pesticides and other pollutants. The potential toxic effects of these pollutant combinations are not fully understood at this time. In order to ensure that diazinon and/or chlorpyrifos are not contributing to a toxic effect in exceedance of our Basin Plan's narrative toxicity objective, the goal of monitoring for these toxic effects was kept in the proposed Basin Plan Amendment. Toxicity testing would be sensitive to antagonistic effects as well as synergistic effects. Mention of antagonistic effects has been added to the discussion under goal 6 in the monitoring section of the Staff Report.

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CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

Amendments to the Water Quality Control Plan For the Sacramento River and San Joaquin River Basins

For

The Control of Diazinon and Chlorpyrifos Runoff into the Sacramento-San Joaquin Delta

June 2006 Final Staff Report

Appendix I

Recommended Format for Comment Letters

Comment letters to the Regional Board on staff recommendations serve two purposes: 1) to point out areas of agreement; and 2) to suggest revisions to staff recommendations. Clear statements of both areas of agreement and suggested revisions will assist the Regional Board and staff in understanding the recommendations of the commenter. In order to aid staff in identifying suggested revisions and to respond to the specific issues raised by the commenter, the following format for comment letters is suggested:

Format for Comments Suggesting Revisions

The suggested format is to number the comment, state in one sentence the topic upon which the comment is directed, provide a supporting argument, and make a specific recommendation. Supporting arguments should include citations, where appropriate. The recommended format is below.

Comment #. *One sentence description or title for the comment*

Suggested revision to the Basin Plan Amendment language or staff report. For suggested revisions to the Basin Plan Amendment language please use underline/strikeout to show changes from the staff proposal. For suggested changes to the staff report, please clearly indicate the section(s) being addressed. The discussion related to the suggested revisions should be clearly supported by reference to applicable law or scientific or technical reports, where appropriate.

Format for Comments Supporting Staff Recommendations

If the commenter concurs with a staff recommendation, a statement to that effect will assist the Regional Board in determining what action, if any, to take on the staff recommendation. In general, no supporting discussion need be presented, unless the commenter feels that the staff recommendation could be further enhanced or clarified. The recommended format is below.

Comment #. *One sentence description or title for the comment*

The provision(s) of the proposed Basin Plan Amendment that the commenter supports should be clearly stated. The commenter may want to provide their reason for supporting the provision of the proposed Basin Plan Amendment, especially if it differs from the staff rationale. Additional legal or scientific citations can also be provided.